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**[Title of the Invention]****Antibacterial and Funginert Ceramics and Manufacturing Method thereof****[Abstract]**

**[Object]** It is an object of the present invention to provide a safe antibacterial and funginert ceramics and a manufacturing method thereof, having superior properties, not only in water resistance, light resistance and heat resistance, but also from a viewpoint of persistency of antibacterial and funginert action and antibacterial and funginert effect.

**[Structure]** An antibacterial and funginert ceramics according to the present invention is manufactured by coating a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, or by further coating the substrate with the titanium oxide film or a platinum film. The anti-bacteria and funginert ceramics manufactured in this manner can effectively prevent propagation of unwanted bacteria and fungus in a solution or on a film because electrons and/or positive holes are generated on the titanium oxide film to perform oxidation-reduction by receiving sunlight, light of lamps or the like as well as an action of the metal ions and is safe and economical and superior in persistency, weather resistance and durability.

**[Claims]**

**[Claim 1]** An antibacterial and funginert ceramics being characterized in that a substrate is coated with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum.

**[Claim 2]** An antibacterial and funginert ceramics being characterized in that a substrate is coated with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, and the substrate is further coated with a platinum film.

**[Claim 3]** An antibacterial and funginert ceramics being characterized in that a substrate is coated with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, and the substrate is further coated with a titanium oxide film.

**[Claim 4]** An antibacterial and funginert ceramics being characterized in that a substrate is first coated with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, and the substrate is further coated with a titanium oxide film and still further coated with a platinum film.

**[Claim 5]** The antibacterial and funginert ceramics according to claim 1 or claims 2, 3 and 4, wherein a substrate coated with an electrically conductive film or an electrically conductive substrate is used as the substrate.

**[Claim 6]** The antibacterial and funginert ceramics according to claim 1 or claims 2, 3 and 4, wherein the titanium oxide film contains 0.0001-10 wt.% of silver or 0.01-15 wt.% of copper, 0.02-20 wt.% of zinc, and 0.01-25 wt.% of platinum.

**[Claim 7]** A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided with an electrically conductive film or an electrically conductive substrate is coated with a titania sol and baked, the substrate is dipped into a solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum, then dried and baked.

**[Claim 8]** A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided with an electrically conductive film or an electrically conductive substrate is coated with a titania sol solution and baked, the substrate is dipped into a solution containing at least one kind of metal ions selected from silver,

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copper, zinc or platinum, then dried and baked, and that the surface of the substrate is further coated with a platinum film.

[Claim 9] A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided with an electrically conductive film or an electrically conductive substrate is coated with a titania sol solution and baked, the substrate is dipped into a solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum and dried, and that the substrate is further coated with a titania sol.

[Claim 10] A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate is coated with a titania sol solution and baked, the substrate is dipped into a solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum and dried, and that the substrate is further coated with a titania sol solution and baked, wherein the surface of the substrate is further coated with a platinum film.

[Claim 11] A method for manufacturing an antibacterial and funginert ceramics being characterized in that a substrate, a substrate provided with an electrically conductive film or an electrically conductive substrate is coated with a titania sol solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum and baked.

[Claim 12] A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided with an electrically conductive film or an electrically conductive substrate is coated with a titania sol solution containing one kind of metal ions selected from silver, copper, zinc or platinum and baked, the surface of the substrate is further coated with a platinum film.

[Claim 13] A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided with an electrically conductive film or an electrically conductive substrate is coated with a titania sol solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum and baked, the substrate is further coated with a titania sol solution and baked.

[Claim 14] A method for manufacturing an antibacterial and funginert ceramics being characterized in that after a substrate, a substrate provided

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with an electrically conductive film, or an electrically conductive substrate is coated with a titania sol solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum and baked, the substrate is further coated with a titania sol solution and baked, and that the surface of the substrate is further coated with a platinum film.

[Detailed Description of the Invention]

[0001]

[Field of Use in Industries]

The present invention relates to an antibacterial and funginert ceramics and a manufacturing method thereof. More particularly, the present invention relates to a safe antibacterial and funginert ceramics, having superior properties, not only in water resistance, light resistance and heat resistance, but also from a viewpoint of maintaining an antibacterial and funginert action and an antibacterial and funginert function, and a manufacturing method thereof.

[0002]

[Prior Art]

It is known from the prior art that an ion of silver, copper, zinc or platinum has an antibacterial and funginert action. However, use of the ion in a liquid condition is inconvenient in handling and there was also a problem in persistency of an antibacterial and funginert effect, durability and safety. An inorganic antibacterial and funginert agent has been recently developed, which can overcome the problem above by allowing a zeolite or montmorillonite being a clay mineral to carry these metal ions (e.g. "Zeolite Vol. 4, 1 (1987)" by Zenji Hagiwara and Sato Ando; "Antibacterial and Funginert Magazine Vol. 19, 425 (1991)" by Tatsuo Yamamoto, Masashi Uchida and Yasuo Kurihara; and "Appl. Clay Sci. Vol. 6, 135 (1991)" by A. Oya, T. Banse, F. Ohashi and S. Otani).

[0003]

However, in the case of the antibacterial and funginert agent of the zeolite system or group, there is a drawback that the antibacterial and funginert effect is small and it is inferior in water resisting properties because the metal ions are carried too strong. On the contrary, in the case of the antibacterial and funginert agent of the montmorillonite system or group, there is a problem in persistency of the antibacterial and funginert effect because carrying or holding force of the metal ions is weak and thus, the

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elution speed thereof is fast. Also, according to the U.S. water quality standard, the ion concentration of silver is 50 ppb or less. It is 100 ppb or less in Germany and 200 ppb in Switzerland. Under these circumstances, the antibacterial and funginert agent of montmorillonite system or group has a problem in the safety and there is also a problem that it changes its color when used.

[0004]

[Problem to be solved by the Invention]

In view of the above-mentioned aspects, it is an object of the present invention to provide an economical antibacterial and funginert ceramics having superior properties not only in the water resistance, heat resistance, light resistance, weather resistance, stability and safety thereof, but also from a viewpoint of persistency of an antibacterial and funginert action and an antibacterial and funginert effect, and the manufacturing method thereof.

[0005]

[Means for solving the Problem]

To attain the object above, an inventor of the present invention has diligently made a study of the inorganic antibacterial and funginert composition. As a result, the present inventor has found that an antibacterial and funginert ceramics manufactured by coating a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, or by further coating the substrate with a titanium oxide film or a platinum film can effectively prevent propagation of unwanted bacteria and fungi in a solution or on a film because electrons and/or positive holes are generated on the titanium oxide film by receiving sunlight, the light from a lamp or the like as well as an action of the metal ions and perform oxidation-reduction. Thus, the inventor has made the present invention.

[0006]

According to the present invention, an antibacterial and funginert ceramics is provided, in which a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate is coated with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, or the substrate is further coated with a titanium oxide film or a platinum film. A method for manufacturing an

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antibacterial and funginert ceramics is provided, in which after a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate is coated with a titania sol solution and baked, the substrate is dipped into a solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum, then dried and baked. A method for manufacturing an antibacterial and funginert ceramics is also provided, in which a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate is coated with a titania sol solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum and baked, wherein the surface of the substrate is further coated with a titania sol solution and baked, or it is coated with a platinum film.

[0007]

The material of substrate to be used in the present invention may be any one of concrete, glass, plastic, ceramics or metal if it has a necessary strength. Also the substrate to be used in the present invention may be transparent or opaque, however the transparent substrate is more convenient because light can permeate through the substrate from the outside.

[0008]

The substrate coated with the electrically conductive film includes one coated with copper or aluminum, or one coated with a transparent conductive film such as tin oxide, ITO (Indium Tin Oxide) or zinc oxide. The method for coating the substrate with the conductive film includes an electrolytic plating method, a CVD method, a PVD method, and a sputtering method.

[0009]

The conductive substrate to be used in the present invention includes metal such as copper, aluminum and titanium, or tin oxide glass, ITO (Indium Tin Oxide) glass and the like. The tin oxide glass and ITO glass are transparent and convenient because light can pass through the substrate from the outside.

[0010]

The substrate to be used in the present invention may take any shape of a prismatic shape, a cylindrical shape, a spherical shape, a conical shape, a guitar-shape, or a rugby ball shape. Also, the substrate may be

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formed in a closed shape or may or may not have a cover. It may be formed in a round tube or a square tube.

**[0 0 1 1]**

The metal ion to be used in the antibacterial and funginert ceramics according to the present invention includes an ion of silver, copper, zinc or platinum, or the metal ions more than two kinds selected among them may also be used.

**[0 0 1 2]**

The titanium oxide film to be used in the present invention may be made by heating/oxidizing a titanium film with gas flame or the like. However, it is more preferable to make the titanium oxide film by preparing first a titania sol solution from alcoxide of titanium which can be obtained through reaction between titanium tetrachloride and alcohol, by coating a substrate with the titania sol solution by means of a dip coating method, a spin coating method, a painting method, a spray thermal decomposition method, etc. and by baking the substrate. The titanium oxide film may also be made by first coating the substrate with a suspension of the titanium oxide having ultra-fine particles using the dip coating method, the spin coating method, the painting method or the spray method, etc., then by baking the substrate. In this case, for the purpose of obtaining a tough titanium oxide film firmly adhered onto the substrate, it is preferable to make the titanium oxide film 0.1 to 0.3  $\mu$ m thick by painting, spraying or spin coating the titania sol solution when the viscosity is small by lowering the concentration thereof, or by decreasing the lifting speed of the substrate. It is desirable that the baking temperature in this case be between 500 °C and 550 °C. It is possible to obtain the thick and tough titanium oxide film by repeating this operation.

**[0 0 1 3]**

The antibacterial and funginert ceramics obtained by coating the substrate with the titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum according to the present invention can be manufactured by dipping the titanium oxide film formed in the above method into a solution in which a metal salt containing at least one kind of metal ions selected from silver, copper, zinc or platinum is dissolved into water and/or an organic solvent and then by baking the titanium oxide film. The antibacterial and funginert ceramics can also be

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manufactured by adding a metal salt solution containing at least one kind of metal ions selected from silver, copper, zinc or platinum to the titania sol solution or a suspension of titanium oxide having ultra-fine particles or by dissolving a metal salt therein, then by coating the substrate with the titania sol solution or the suspension added or dissolved above by means of the dip coating method, the spin coating method, the painting method, the spray thermal decomposition method, etc. and baking the substrate. In this case, it is possible to change the concentration of metal ions of silver, copper, zinc or platinum contained in the antibacterial and fungicidal ceramics by changing the concentration of the metal salt solution, an amount of the metal salt or the number of times of coating and baking by the dip coating method, the spin coating method, the painting method, the spray thermal decomposition method, etc. onto the substrate. The metal salt used herein includes various salts, for example, a halide such as sulfate, nitrate, carbonate, acetate, ammonium salt, chloride and bromide; and an organic salt such as stearate and acetate, but it should not be limited to these. The metal salt may be anhydrous salt, hydrate salt or the mixture thereof. It may also be a mixture of silver salt, copper salt, zinc salt or platinum salt.

[0014]

The antibacterial and fungicidal ceramics obtained by coating the substrate with the titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum according to the present invention and by further coating the substrate with another titanium oxide film can be manufactured by coating the substrate of the antibacterial and fungicidal ceramics coated with the titanium oxide containing at least one kind of metal ions selected from silver, copper, zinc or platinum manufactured by the method mentioned above with a titania sol solution or a suspension of titanium oxide having ultra-fine particles by means of the dip coating method, the spin coating method, the painting method or the spray thermal decomposition method, etc. and then by baking the substrate. In this case, it is possible to adjust the thickness of the titanium oxide film provided on the surface of the substrate by changing the number of times of coating and baking by the dip coating method, the spin coating method, the painting method, the spray thermal decomposition method or the like onto the substrate. In this manner, it is possible to properly adjust the release speed of the metal ions of silver, copper, zinc or platinum and an effective



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time-period of the antibacterial and funginert ceramics so that the concentration of metal ions in the water does not exceed the water quality standard.

[0015]

The concentration of metal ions used in the antibacterial and funginert ceramics according to the present invention is 0.0001 ~ 10 wt.% for silver, 0.01 ~ 15 wt.% for copper, 0.02 ~ 20 wt.% for zinc and 0.01 ~ 25 wt.% for platinum, relative to the titanium oxide film. If each concentration is less than the above figure, the antibacterial and funginert effect is weak, while if the concentration is greater than the figure, an amount of elution of the metal ions becomes large. An optimum amount of the concentration of metal ions used in the antibacterial and funginert ceramics can be determined depending on the use period and/or a degree of the antibacterial and funginert effect needed.

[0016]

Also, a method for coating the surface of the substrate with the platinum film to be used in the present invention includes a photo-electrodeposition method, a CVD method, a PVD method, a sputtering method, etc. It is also possible to properly adjust the release speed of metal ions of silver, copper, zinc or platinum and/or an effect of the antibacterial and funginert ceramics by adjusting the thickness of the platinum film. The concentration of metal ions in the water can also be adjusted so that it does not exceed the water quality standard.

[0017]

The antibacterial and funginert ceramics, according to the present invention, obtained in this manner, can effectively prevent propagation of unwanted bacteria and fungi in a solution or on a film by the oxidation-reduction action of the electrons and positive holes generated on the titanium oxide film by receiving sunlight, light from lamp or the like as well as an action of the antibacterial and funginert metal ions such as silver. Accordingly, if such an antibacterial and funginert ceramics is applied to the tiles which are attached to the inside of a swimming pool, it is possible to prevent swimmers from slipping and falling on the bottom or wall of the pool slimy with sliminess. If it is applied to the tiles of a bathroom and/or an outer wall of a building, it is possible to prevent generation of blackening due to fungi etc. If it is applied to a vessel for containing a drinking water etc., it is

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possible to prevent propagation of unwanted bacteria and rotting thereof and to keep the drinking water etc. for a long time at room temperature. Further, if the substrate is in the form of a thin film or sheet, or a fabric, it can be used as clothes, medical articles or a wrapping pouch. The antibacterial and funginert ceramics according to the present invention can also be widely applied to, for example, duckboards, a bath-tub, a bath, tiles of a fountain, a sink, a triangular corner of a sink, a handrail of a pool or a bathroom, a washbowl, a chopping-board, a washing stand, a showcase for fishes, medical instruments, shoes, slippers, a water tank of a humidifier, a shaver, a carpet, or the like.

[0018]

[Embodiments]

Representative examples of the embodiments according to the present invention will now be described hereunder.

[0019]

**Embodiment 1**

0.1 mol of titanium isopropoxide is diluted by 100 ml of anhydrous ethanol, then 2.7 ml of 2 normal hydrochloric acid is added to the diluted titanium isopropoxide while stirring the latter to prepare a transparent sol liquid, thereby coating a slide glass substrate with a titanium oxide film by means of a dip coating method. The slide glass substrate is dipped into the sol liquid, then lifted up and dried, wherein it was baked at a temperature of 400 °C. After repeating this operation twenty (20) times, the slide glass substrate is baked at a temperature of 550 °C and as a result, a titanium oxide film of about 4  $\mu$ m thickness was formed on the slide glass substrate. The slide glass substrate is dipped in a solution of silver nitrate of 0.5 mol/l, then lifted up and dried. The substrate is then dipped again into the sol liquid, wherein five layers of titanium oxide was coated on the substrate by means of the dip coating method. The antibacterial and funginert effect of the antibacterial and funginert ceramics obtained in this manner was examined by the following method. First, unwanted bacteria collected from a food processing machine was put under stationary culture for 24 hours at a culture medium of meat extra bouillon. 1 ml of bacteria liquid obtained in this manner was dripped at two (2) positions on a sample. a membrane filter is put on bacteria liquid dripped and the stationary culture was performed for 24 hours at a temperature of 37 °C. Then, phosphoric acid buffer

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solution was added to the bacteria liquid and shaken. After this, 1 ml of the bacteria liquid was taken out, wherein the number of living bacteria was measured by means of a pour-plate culture method. As a result, the number of living bacteria has decreased to almost zero (0). Thus, obtaining 99.9% of sterilization ratio was obtained compared with a blank test conducted using a mere slide glass.

**[0020]****Embodiment 2**

125 ml of titanium isopropoxide is added to 20 ml of isopropyl alcohol and they are dripped into 750 ml of distilled water while stirring. 5 g of silver nitrate, 12g of zinc nitrate 6 hydrate and 6 ml of 70% nitric acid were also added to the distilled water. This solution was heated at a temperature of 80 °C for eight (8) hours to prepare a transparent sol liquid, wherein a titanium oxide film was coated on a substrate of tin oxide glass by means of a spin coating method. First, this sol liquid is dripped on the tin oxide glass substrate while rotating the substrate at a speed of 800 rpm, then dried and baked at a temperature of 400 °C. After repeating this operation twenty (20) times, the tin oxide glass substrate was baked at a temperature of 550 °C to form a titanium oxide film of a thickness of about 5 µm thereon. This is dipped into an ethanol water solution of 2g/l of potassium platinichloride, and the light of 100 W mercury lamp is irradiated on this titanium oxide film for four (4) hours while stirring the solution by means of a magnetic stirrer, thereby coating platinum on the surface of the titanium oxide film by means of a photo-electrodeposition method. An antibacterial and fungicidal effect of the antibacterial and fungicidal ceramics obtained was examined by the following method. First, 1 ml of bacterial liquid of staphylococcus or colibacillus cultivated on a culture medium of meat extract bouillon is dripped at two (2) positions on a sample. A membrane filter is put on the surface of sample and a stationary culture was performed at a temperature of 37 °C for 24 hours. Thereafter, a phosphoric acid buffer solution was added and shaken, and then 1 ml of the bacterial liquid is taken out, wherein the number of living bacteria was measured by means of the pour-plate culture method. As a result, the sterilization ratio of 99.2% was obtained in the case of staphylococcus, or the sterilization of 94.2% in the case of colibacillus, compared with a blank test conducted using a mere tin oxide glass.

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[0021]

**Embodiment 3**

125 ml of titanium isopropoxide is added to 20 ml of isopropyl alcohol and dripped into 750 ml of distilled water while stirring. After this, 20g of copper sulfate 5 hydrate and 5 ml of 70% hydrochloric acid were added. This solution was heated at a temperature of 80 °C for eight (8) hours to prepare a transparent sol liquid. After applying the sol liquid to a washbowl or washbasin made of metal by a brush, it was dried and baked at a temperature of 300 °C. After repeating this operation fifteen (15) times, the same operation was repeated five (5) times using a transparent sol liquid produced without adding the copper sulfate, and the washbowl or washbasin was baked at a temperature of 500 °C. Water of a goldfish basin was poured into the washbowl obtained in this manner and was left for one month under a fluorescent lamp. However, no sliminess was generated on the surface thereof and the water remained clean without producing unwanted bacteria and/or algae therein. When a metal washbasin on which the titanium oxide film has not been coated is used, algae came out in a week and sliminess was found. Water started to get muddy.

[0022]

**Embodiment 4**

A transparent and colorless glass bead coated with a transparent conductive film of ITO is coated first with a titanium oxide film containing copper sulfate in the same manner as in the embodiment 3 and then coated further with another titanium oxide film. The glass bead was then dipped into an ethanol water solution of 2g/l of potassium platinichloride and irradiated with the light of 100 W mercury lamp for four (4) hours while stirring the solution by means of a magnetic stirrer, thereby coating the surface of the titanium oxide film with platinum by means of a photo-electro deposition method. A spherical antibacterial and funginert ceramics obtained herein is put into a transparent glass bottle containing natural clear water was left in a well-lighted place for one (1) month. As a result, the water becomes muddy and unwanted bacteria started to propagate in the glass bottle when no spherical antibacterial and funginert ceramics was put therein, but the water remain transparent and unwanted bacteria were scarcely detected in the bottle when the spherical antibacterial and funginert ceramics was put in the bottle.

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**[0023]****Embodiment 5**

125 ml of titanium isopropoxide is added to 20 ml of isopropyl alcohol and it was then dripped into 750 ml of distilled water while stirring, wherein 6 ml of 70% nitric acid was also added thereto. This solution was heated at a temperature of 80 °C for eight (8) hours to prepare a transparent sol liquid, wherein a titanium oxide film was coated on a white ceramic tile 20 times (i.e. 20 layers) by means of the dip coating method in the same manner as in the embodiment 1. This ceramic tile is first dipped into an aqueous solution containing 200g/l of zinc chloride and 5g/l of potassium platinichloride and lifted up and dried. Then, the titanium oxide film was further coated on the ceramic tile six (6) times (i.e. 6 layers) by means of the dip coating method in the same manner as the above. The antibacterial and funginert ceramic tiles obtained in this manner were attached to a wall of a pond, which was then filled up with water. Though they were left in the pond as they are for two (2) months, but no aliminess was generated on the tiles.

**[0024]****Embodiment 6**

A transparent and colorless glass bead of 5 mm in diameter, after being sprayed with a transparent sol liquid prepared in the same manner as in the embodiment 1, is dried and baked at a temperature of 350 °C. After repeating this operation twenty (20) times, the glass bead was baked at a temperature of 500 °C. After this, the glass bead was dipped into 100 ml of aqueous solution containing 15 g of silver nitrate, 20 g of copper nitrate 6 hydrate, and 25 g of zinc nitrate 6 hydrate, then it was lifted up and dried. After spraying the sol liquid on the glass bead and drying, it was baked at a temperature of 350 °C. After repeating this operation five (5) times, the glass bead was baked at a temperature of 500 °C, then put into an ethanol water solution of 2g/l of potassium platinichloride, wherein the glass bead was irradiated with the light of 100 W mercury lamp for four (4) hours while stirring the solution by means of a magnetic stirrer, thereby coating platinum on the surface of the titanium oxide film by means of the photo-electrodeposition method. The antibacterial and funginert effect of the antibacterial and funginert ceramics obtained in this manner was examined by the following method. First, unwanted bacteria collected from a food processing machine were put under stationary culture for 24 hours on a

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culture medium of meat extract bouillon, and 5 ml of the bacteria liquid obtained is put into 70 ml of phosphoric acid buffer solution in which the spherical antibacterial and funginert ceramics obtained has been put and shaken, thereby conducting shake culture. Twenty-four (24) hours later, 1 ml of the bacteria liquid was taken out for measurement of the number of living bacteria by means of the pour-plate culture method. As a result, the sterilization ratio of 97% was obtained compared with a blank test conducted using a mere glass bead. Also, when light of an incandescent lamp are irradiated during shake culture, the sterilization ratio improved to 98%.

[0025]

**Embodiment 7**

After adding 400 g of isopropyl alcohol to 2.5 kg of titanium isopropoxide, it was dripped into 15 kg of distilled water while stirring, wherein 100 g of silver nitrate and 120 ml of 70% hydrochloric acid were added to the water and then heated at a temperature of 80 °C for twenty-four (24) hours. A chopping board made of alumina was dipped into a transparent sol liquid obtained, wherein a titanium oxide film was coated on the chopping board fifteen (15) times (i.e. 15 layers) by means of the dip coating method in the same manner as in the embodiment 1. And, the surface of the chopping board was coated with a transparent sol liquid five (5) times (i.e. 5 layers) in the same manner as the above and baked at temperature of 500 °C. The antibacterial and funginert chopping board obtained herein was used for two (2) months, but no fungi or propagation of unwanted bacteria or change of color was acknowledged on the surface thereof. Also, the antibacterial and funginert chopping board obtained herein was dipped into a water for two (2) days, but the concentration of silver ion in the water was 10 ppb or less which is lower than the water quality standard.

[0026]

**[Effect of the Invention]**

As described above, the present invention has an object to provide an economical antibacterial and funginert ceramics and a manufacturing method thereof, having superior properties, not only in water resistance, heat resistance, light resistance, weather resistance, stability, and safety, but also from a viewpoint of persistency of antibacterial and funginert action and antibacterial and funginert effect. The antibacterial and funginert

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ceramics manufactured by coating a substrate, a substrate provided with an electrically conductive film, or an electrically conductive substrate with a titanium oxide film containing at least one kind of metal ions selected from silver, copper, zinc or platinum, or by further coating the substrate with a titanium oxide film or a platinum film can effectively prevent propagation of unwanted bacteria and fungi in the solution or on the film because electrons and/or positive holes generated on the titanium oxide film perform oxidation-reduction by receiving sunlight, light of lamp or the like as well as the action of metal ion. Accordingly, if this is applied to the tiles which can be attached to the inside of a swimming pool, it is possible to prevent swimmers from easily slipping because of sliminess generated on the bottom or wall of the pool. If this ceramics is applied to the tiles of a bathroom or an outer wall of a building, it is possible to prevent possible blackening due to fungi etc. Further, if this ceramics is applied to a vessel for storing drinking water etc., it is possible to store the water etc. for a long time at room temperature because it can prevent propagation and/or rotting of unwanted bacteria. If the substrate is in the form of a thin film, a sheet or fabrics, it can also be used as clothes, medical articles or a wrapping pouch. The titanium oxide used in present invention is used in the paint, cosmetics, tooth powder or the like. Since the antibacterial and funginert ceramics according to the present invention has an advantage that it is superior in the weather resistance and durability, and nonpoisonous and safe, it is superior in water resistance, heat resistance, light resistance, weather resistance, stability and safety. The antibacterial and funginert ceramics according to the present invention can also be widely applied, for example, to duckboards, a bath-tub, tiles of a fountain, a sink, a triangular corner of the sink, a handrail of a pool or a bathroom, a washbowl, a chopping-board, a washing stand, a showcase for fishes, medical instruments, shoes, slippers, a water tank or an outlet nozzle of a humidifier, a shaver, a carpet or the like.

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ACCESSION NUMBER: 1994-115109 [14] WPINDEX

DOC. NO. CPI: C1994-053172

TITLE: Antifungal, antibacterial ceramic with good heat resistance - comprises conductive substrate with titanium oxide coating film contg. silver, copper, zinc and/or platinum ions.

DERWENT CLASS: D22 E32 L02

PATENT ASSIGNEE(S): (AGEN) AGENCY OF IND SCI & TECHNOLOGY

COUNTRY COUNT: 1

PATENT INFORMATION:

PATENT NO	KIND	DATE	WEEK	LA	PG	MAIN	IPC
JP 06065012	A	19940308	(199414)*		6	A01N059-16	<--
JP 07037363	B2	19950426	(199521)		6	A01N059-16	

APPLICATION DETAILS:

PATENT NO	KIND	APPLICATION	DATE
JP 06065012	A	JP 1992-242640	19920819
JP 07037363	B2	JP 1992-242640	19920819

FILING DETAILS:

PATENT NO	KIND	PATENT NO
JP 07037363	B2 Based on	JP 06065012

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MAIN: A01N059-16

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BASIC ABSTRACT:

JP 06065012 A UPAB: 19940524  
Ceramic comprises a substrate and a titanium oxide film contg. at least one metal ion selected from silver, copper, zinc and platinum. The ceramic pref. further comprises a Pt film or a titanium oxide film covering the titanium oxide film contg. the metal ion. The ceramic pref. further comprises a titanium oxide film covering the titanium oxide film contg. the metal ion, and a Pt film coating the titanium oxide film. A substrate having a conductive coat or a conductive substrate is used as the substrate.

The ceramic pref. contains 0.0001-10 wt.% silver, 0.01-15 wt.% copper, .02-20 wt.% zinc and 0.01-25 wt.% platinum to the titanium oxide film.

Prodn. comprises coating a titania sol. on a substrate (a substrate coated with a conductive film, or a conductive substrate), firing it, immersing in a soln. contg. at least one metal ion selected from silver, copper, zinc and platinum followed by drying, and firing.

USE/ADVANTAGE - Safe antifungal, antibacterial ceramic showing high water resistance, light resistance and heat resistance is provided. The ceramic has long-lasting antifungal and antibacterial properties.

In an example, 0.1 mol titanium isopropoxide is diluted in 100 ml of



anhydrous ethanol and 2.7 ml of hydrochloric acid (2N) was added while stirring to prepare a transparent soln., which is then coated on a slide glass by dip-coated process. After drying, it was fired at 400 deg. C, and the process was repeated 20 times, then fired at 550 deg. C to provide a titanium oxide film of about 4 microns on the slide glass substrate. Then it was dipped in 0.5 mol.1 silver nitrate aq. soln. and dried, then dipped in the soln. so that the titanium oxide film (5 layers) was coated.

Dwg.0/0

FILE SEGMENT:

CPI

FIELD AVAILABILITY:

AB; DCN

MANUAL CODES:

CPI: D09-A01A; D09-A01C; E35-A; E35-B; E35-C; E35-K02;  
E35-X; L02-A; L02-G01